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(54) Title: GERMANIUM DOPED SILICA FORMING FEEDSTOCK AND METHOD

(57) Abstract

The present invention is directed to a silica forming feedstock and a method of making optical wageguides and optical waveguide preforms. The feedstock for use in the manufacturing of germanium doped silica glass products includes a siloxane and a germanium dopant component such as germanium alkoxide. The invention further relates to the manufacturing of optical waveguides and optical waveguide preforms using a fluid feedstock which includes a siloxane and germanium dopant component preferably germanium alkoxide.

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GERMANIUM DOPED SILICA FORMING FEEDSTOCK AND METHOD

FIELD OF THE INVENTION

The present invention relates to silica feedstock compositions. More particularly, the present invention relates to silica forming feedstocks, and the manufacturing of optical waveguide preforms.

BACKGROUND OF THE INVENTION

Various processes are known that involve the production of metal oxides from a variety of feedstocks. Such processes require a feedstock and a means of catalyzing oxidation and combustion of the feedstock to convert the feedstock into finely divided aggregates called soot. This soot can be collected on deposition surfaces, ranging from a collection chamber to a rotating mandrel. The soot may be simultaneously or subsequently heat treated to form a high purity glass article. This process is usually carried out using specialized conversion site equipment having an arrangement of delivery tubes and flame generating burners.

Much of the initial research that led to the development of such processes, including flame hydrolysis, focused on the production of silica glass products such as bulk fused silica. Selection of an appropriate feedstock which can be converted into the desired silica glass

composition is an important aspect of such research. Commercial production of silica glass by such a conversion process became and is continued to be dominated by the use of silicon tetrachloride ($SiCl_4$) as the feedstock's source of silicon. The high vapor pressure of silicon tetrachloride and its purity has made it a useful and convenient source of vapor for conversion into SiO_2 soot. This use of silicon tetrachloride provides a high purity silica glass and has been the commercially preferred method of manufacturing silica glass for use in optical waveguide products and particularly the manufacturing of optical waveguide fibers and their preforms. Such use of silicon tetrachloride in the manufacturing of optical waveguides has led to the adoption of other similar chloride-based feedstocks which are compatible and used in conjunction with silicon tetrachloride to provide beneficial silica glass compositions and corresponding indexes of refraction which are able to guide light. The silica glass dopant feedstock vapor $GeCl_4$ is used in conjunction with $SiCl_4$ vapors to form silica glass compositions doped with appropriate levels of germanium dioxide which are utilized in the manufacturing of optical waveguides. This has led to the presently accepted use of $SiCl_4$ vapors and $GeCl_4$ vapors in the manufacturing of optical waveguide silica glass cores doped with GeO_2, even though such feedstocks result in the production of hazardous by products such as hydrochloric acid (HCl).

In light of this, there is a need for a germanium doped silica feedstock and a method of forming optical waveguide preforms which results in an optical waveguide product such as an optical fiber while avoiding the hazardous by products of the prior art.

SUMMARY OF THE INVENTION

Accordingly, the present invention is directed to a silica forming feedstock and method of forming optical waveguides and optical waveguide preforms that substantially obviates one or more of the problems due to limitations and disadvantages of the related art.

The principal advantage of the present invention is to provide a silica forming feedstock which produces a germanium doped silica glass which allows for the manufacturing of optical waveguides and preforms thereof without the production of hazardous halides.

Additional features and advantages of the invention will be set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objectives and other advantages of the invention will be realized and attained by the methods and compositions of the invention particularly pointed out in the written description and claims hereof as well as the appended drawings.

To achieve these and other advantages in accordance with the purpose of the invention, as embodied and broadly described, the invention is a fluid feedstock including siloxane and a germanium compound.

In another aspect, the invention includes a method of using the inventive feedstock in the formation of optical waveguide preforms and optical waveguides.

In a further aspect, the invention includes the making of optical waveguide preforms, which are predecessors and physical embodiments of an optical waveguide product prior to the final forming of the preform into the optical waveguide product, such as by drawing a preform into an optical waveguide fiber.

In another aspect, the invention includes the forming of optical waveguide preforms by such processes as

cladding, drying, consolidating, stretching, caning, overcladding, and reconsolidating.

In a further aspect, the invention includes a method of making low loss optical fiber by converting a siloxane and germanium alkoxide feedstock into a GeO_2 doped silica glass.

In another aspect, the invention includes an optical waveguide silica feedstock and an optical fiber silica feedstock which includes a siloxane and a germanium alkoxide.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are intended to provide further explanation of the invention as claimed.

The accompanying drawings are included to provide a further understanding of the invention and are incorporated in and constitute a part of this specification, illustrate embodiments and aspects of the invention and together with the description serve to explain the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 comprises a schematic representation of the method and apparatus set up of the invention.

FIG. 2 is a refractive index profile of an optical waveguide preform in accordance with the teachings of the present invention, with the Y-axis representing the index of refraction of the preform and the X-axis representing the radius of the preform.

FIG. 3 is a plot of the spectral attenuation of an optical waveguide in accordance with the teachings of the

present invention, with the Y-axis representing Loss (dB/km) and the X-axis representing Wavelength (nm).

FIG. 4 is a plot of the spectral attenuation of an optical waveguide in accordance with the teachings of the present invention, with the Y-axis representing Loss (dB/km) and the X-axis representing Wavelength (nm).

DETAILED DESCRIPTION OF THE INVENTION

Reference will now be made in detail to the present preferred embodiments of the invention, examples of which are illustrated in the accompanying drawings.

The silica forming feedstock of the invention includes a siloxane and a germanium alkoxide. Preferably, the siloxane component of the feedstock fluid is a polyalkysiloxane, more preferably a cyclic polyalkysiloxane, and most preferably octamethylcyclotetrasiloxane $[SiO(CH_3)_2]_4$. The preferred germanium alkoxide is germanium ethoxide $[Ge(OC_2H_5)_4]$. Germanium ethoxide and octamethylcyclotetrasiloxane are both liquids at standard atmospheric pressure and room temperature.

Germanium alkoxide and siloxane are mixed in proportions to provide a target GeO_2 dopant concentration desired in the silica soot. Such a GeO_2 dopant concentration gives the glass, and usually in the waveguiding core formed from the glass, a refractive index appropriate for guiding light when the GeO_2 doped glass is cladded with a glass having a different refractive index, usually silica glass. When germanium ethoxide and octamethylcyclotetrasiloxane are used they are mixed by weight in a ratio ranging from 1 part $Ge(OC_2H_5)_4$: 2 to 4 parts $[SiO(CH_3)_2]_4$, with the preferred weight ratio of the feedstock mixture being 1 part $Ge(OC_2H_5)_4$: 3 parts $[SiO(CH_3)_2]_4$.

The use of octamethylcyclotetrasiloxane with germanium alkoxides, in particular germanium ethoxide, as the feedstock mixture of the invention is preferred because of the compatibility of these two compounds when used in practicing the invention. During the practicing of the invention germanium ethoxide and octamethylcyclotetrasiloxane liquids were mixed together in a normal air atmosphere without any evidence of reaction and the mixture remained clear. In addition, the two compounds are compatible in that the conditions of a conversion flame are suitable for the formation of GeO_2 doped SiO_2 soot. The co-combustion of the germanium ethoxide vapor and the octamethylcyclotetrasiloxane vapor in a flame provide for GeO_2 doped SiO_2 with GeO_2 concentrations greater than 8 wt.% and soot densities less than 0.6 g/cc, both of which are preferred in the production of optical fiber by outside vapor deposition. High concentrations of GeO_2 doping, such as 30 wt.% GeO_2, are achievable using the compositions of the invention. It has been found that the collection efficiency of GeO_2 is dependent on the amount of octamethylcyclotetrasiloxane present in the flame with the germanium ethoxide. In preferred embodiments octamethylcyclotetrasiloxane and O_2 levels are used to favor the GeO_2/GeO equilibrium to the production of GeO_2.

The silica forming feedstocks of the invention based on siloxane and germanium alkoxide range from:

1 to 99 wt.% germanium alkoxide and 1 to 99 wt.% siloxane;

more preferably 14 to 35 wt.% germanium alkoxide and 65 to 86 wt.% siloxane; and

most preferably 18 to 30 wt.% germanium alkoxide and 70 to 82 wt.% siloxane,

with the preferred germanium alkoxide being germanium ethoxide and the preferred siloxane being octamethylcyclotetrasiloxane.

These feedstock compositions should be used in the making of optical waveguides and optical waveguide preforms with the following burner condition ranges of:

Delivery rate of feedstock mixture:	3 to 12 g/min
Total burner O_2:	4 to 20 slpm
Carrier N_2:	0.5 to 2.4 slpm
Inner Shield N_2:	2.5 to 3.5 slpm

and the understanding that the overall burner stoichiometry should be greater than 0.8, the premix flow should be kept low to minimize the flame temperature to achieve a high GeO_2 retention level, such as $CH_4 + O_2$ premix < 4 slpm, and minimize the carrier N_2 and inner shield N_2 flow rates while maintaining a constant feedstock vapor flow and inhibiting the fume stream from touching down on the burner face.

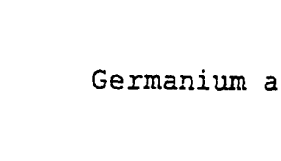
In addition to utilizing germanium alkoxides, such as germanium ethoxide and germanium methoxide, for the germanium dopant source compound of the feedstock, the germanium dopant source compounds include:

bimetallic organogermyls such as digermanes (Ge-Ge) and di-germoxanes (Ge-O-Ge);

germanium alkylalkoxides; and

germanium alkyls.

Digermanes, such as hexamethyldigermane, and di-germoxanes, such as hexamethyldigermoxane, which are compatible with siloxanes may be used in the silica forming feedstock.

Germanium alkylalkoxides,  ,

such as (acetyloxy)triethylgermane, which are compatible with siloxanes may be used in the silica forming feedstock.

Germanium alkyls, $R' - \underset{\displaystyle R'''}{\overset{\displaystyle |}{Ge}} - R$,

such as tetraethylgermane, which are compatible with siloxanes may be used in the silica forming feedstock.

An exemplary schematic representation of the method of making an optical waveguide preform utilizing the inventive feedstocks is shown in FIG. 1.

As shown in FIG. 1, the method of the invention includes the step of providing a silica forming fluid feedstock 10, preferably comprised of a siloxane and a germanium alkoxide. Germanium alkoxide and siloxane in liquid form are mixed together to form feedstock 10 and stored in storage container 12. The method of the invention further includes the step of delivering fluid feedstock 10 to a conversion site 29 as shown in FIG. 1. Fluid feedstock 10 is kept under a dry nitrogen atmosphere to prevent hydrolyzation. Teflon tubing is utilized in the liquid feedstock delivery system to preserve the feedstock's high purity. The feedstock is delivered to flash vaporizer 14 at a controlled rate by controllable pump 16 through teflon tubing conduits 18 Flash vaporizer 14 is comprised of a machined aluminum block which is held at an elevated temperature, preferably in the range of 180°-185°C, so that the liquid feedstock is immediately vaporized on contact with the vaporizer at the controlled rate of delivery. The mixed vapors of germanium alkoxide and siloxane are delivered to burner 22 through vapor delivery conduit 24 made of stainless steel along with a nitrogen carrier gas supplied from N_2 carrier gas supply 20. The N_2 gas delivery flow rate and the flow rate of other gas delivery systems of the invention are controlled by gas flow controllers 21 as shown in FIG. 1. Gas flow controllers 21 can be mass flow controllers and

other flow regulators. Oxygen is added to the germanium alkoxide, siloxane, and nitrogen vapor mixture just prior to being delivered to burner 22, from fume O_2 source 26 through flow controller 21 and conduit 25.

Conduits 24 and 25 are heated to greater than 185°C in order to maintain the vapor state of the feedstock.

An alternative method of delivery may be used wherein the liquid feedstocks of germanium alkoxide and siloxane are stored in separate storage containers and delivered to separate vaporizers. The feedstock vapors produced by such separate vaporizers are then mixed together in the vapor delivery conduit prior to delivery to the burner. In addition, the feedstock components could be delivered separately to a mixing chamber and then to a vaporizer or mixed at the vaporizer. In addition, the feedstock mixture and its components can be utilized in a liquid delivery system as disclosed in U.S. Provisional Application Number 60/008,889 by Hawtof et al., the disclosure of which is herein incorporated by reference.

The method of the invention further includes the step of converting the delivered fluid feedstock into GeO_2 doped SiO_2 soot.

As shown in FIG. 1, the fluid mixture of germanium alkoxide, siloxane, nitrogen and oxygen vapors are delivered through the central fume tube of gas-oxy focus burner 22 to conversion site flame 28 where the feedstock is converted to GeO_2 doped SiO_2 soot. The central tube of focused burner 22 is surrounded by oxygen inner shield regulated supply 30, then methane and oxygen premix regulated supply 32, and then oxygen outer shield regulated supply 34 which are used to control the characteristics of conversion flame 28 and the converting of the germanium alkoxide and siloxane vapor feedstock into GeO_2 doped SiO_2 soot which is deposited on the

deposition surface of a polycrystalline alumina bait rod 36.

An alternative method of converting the feedstock is to use a gas-oxy focus burner configuration wherein the fluid feedstock, N_2, and O_2 mixture is delivered through the central fume tube which is surrounded by a N_2 inner shield regulated supply, then a fume shield O_2 regulated supply, then a methane and oxygen premix regulated supply. The N_2 inner shield regulated supply gas lines and the fume shield O_2 regulated supply gas lines should be heated in order to inhibit build up on the burner face.

The method of the invention includes the step of depositing the GeO_2 doped SiO_2 soot on a deposition surface. The GeO_2 doped SiO_2 soot is deposited and collected on the deposition surface of bait rod 36 to form the preform of an optical waveguide core. When a sufficient amount of GeO_2 doped SiO_2 soot is deposited on the deposition surface to form an optical waveguide core, the delivery of the germanium alkoxide and siloxane fluid feedstock mixture to burner 22 is halted.

The method of the invention further includes the step of forming the deposited GeO_2 doped SiO_2 soot into an optical waveguide preform. Siloxane fluid 11 is delivered to burner 22 in place of feedstock mixture 10 in order to form a cladding over the deposited GeO_2 doped SiO_2 soot. Siloxane feedstock delivery system 38 operates in the same manner as the germanium alkoxide and siloxane vapor feedstock mixture delivery system but only delivers siloxane, preferably octamethylcyclotetrasiloxane, O_2, and N_2 to burner 22 which is converted at conversion site 29 by flame 28 into undoped SiO_2 soot. This undoped SiO_2 soot is deposited over the GeO_2 doped SiO_2 soot to form the preform of the optical waveguide cladding.

After a sufficient amount of undoped SiO_2 soot is deposited over the GeO_2 doped SiO_2 soot, the deposition of

soot is halted. The porous soot optical waveguide preform which has formed around the bait rod is removed from the bait rod. The porous soot preform is dried in a helium and chlorine atmosphere and sintered into a clear, fully dense consolidated glass cylindrical optical waveguide preform that is comprised of a GeO_2 doped silica waveguiding core structure surrounded by a silica cladding structure. This consolidated preform is stretched into an optical waveguide cane preform. This preform is overcladded with additional undoped silica soot such as produced by siloxane feedstock delivery system 38 during the formation of the cladding soot. An alternative method is to overclad the preform with undoped silica soot produced by the flame hydrolysis of $SiCl_4$.

The overcladded preform is reconsolidated and may be drawn into an optical waveguide fiber.

Example 1

An optical waveguide preform was formed using the setup of FIG. 1 and then drawn into an optical waveguide fiber. The silica forming feedstock 10 comprised a mixture of 1 part by weight of germanium ethoxide and 3 parts by weight of octamethylcyclotetrasiloxane and was stored in storage container 12. Feedstock 10 was pumped by controllable pump 16 to flash vaporizer 14 at 3.6 grams per minute where feedstock 10 was vaporized. In forming the fiber core, the vaporized feedstock 10 was delivered to burner 22 by a N_2 carrier gas flow of 2.4 slpm (standard liters per minute) supplied by carrier N_2 supply 20. Fume O_2 was added to the vaporized feedstock mixture just prior to the burner by O_2 fume source 26 at 4.5 slpm.

The vaporized feedstock was converted in flame 28 into GeO_2 doped SiO_2 soot and deposited on bait rod 36. Flame 28 was maintained by the supply of 2.5 slpm of O_2 by inner O_2 shield supply 30, 2.0 slpm of CH_4 and 1.0 slpm of

O_2 by CH_4+O_2 premixed supply 32, and 2.0 slpm of O_2 by outer O_2 shield supply 34.

These delivery rates were maintained for 150 minutes and 22 grams of GeO_2 - SiO_2 soot were deposited on bait rod 36 to form the core of the optical fiber preform.

Then SiO_2 soot was deposited over this GeO_2 - SiO_2 soot to form the cladding of the preform. 4.0 grams per minute of octamethylcyclotetrasiloxane were delivered from octamethylcyclotetrasiloxane storage container 40 through pump 42 to flash vaporizer 44. Vaporized octamethylcyclotetrasiloxane was delivered to burner 22 by a N_2 carrier gas flow of 2.4 slpm supplied by carrier N_2 supply 20. 3.5 slpm of fume O_2 was added to the vaporized octamethylcyclotetrasiloxane just prior to burner 22 by O_2 fume source 26. This vaporized octamethylcyclotetrasiloxane flow was converted in flame 28 into SiO_2 soot and deposited on top of the GeO_2 - SiO_2 soot. Flame 28 was maintained by the supply of 3.0 slpm of O_2 by inner O_2 shield supply 30, 2.0 slpm of CH_4 and 1.0 slpm of O_2 by CH_4 + O_2 premixed supply 32, and 2.0 slpm of O_2 by outer O_2 shield supply 34. These delivery rates were maintained for 300 minutes and 285 grams of soot were deposited.

Following this laydown of SiO_2 soot over the GeO_2 - SiO_2 soot, the bait rod was removed, the preform was dried in a helium-chloride atmosphere, consolidated and stretched into a glass cane preform. This glass cane preform was then overcladded with additional SiO_2 soot. This overcladding of the preform was done in the same manner as the SiO_2 soot deposition over the GeO_2 - SiO_2 soot except that, 7.0 grams per minute of octamethylcyclotetrasiloxane were delivered by 2.4 slpm of N_2 carrier with 6.0 to 5.5 slpm of fume O_2 added just prior to the burner. Flame 28 was maintained by 3.5-4.0 slpm of inner shield O_2, 2.0 slpm of CH_4 and 1.0 slpm of O_2 to CH_4 + O_2 premix, and 2.0 slpm of outer shield O_2. These delivery rates were

maintained for 270 minutes and 463 grams of soot were deposited. This overcladded core/clad cane preform was then reconsolidated into a preform which was drawn into a single-mode optical waveguide fiber.

These germanium ethoxide, octamethylcyclotetrasiloxane, and oxygen delivery rates are preferred in order to provide for the complete combustion of the germanium ethoxide and octamethylcyclotetrasiloxane in accordance with the following reactions:

$$Ge(OC_2H_5)_4 + 12O_2 = GeO_2 + 8CO_2 + 10H_2O$$

$$[SiO(CH_3)_2]_4 + 16O_2 = 4SiO_2 + 8CO_2 + 12H_2O$$

These preferred delivery rates provide a burner oxygen stoichiometry greater than 0.8, wherein stoichiometry is defined as the ratio of total oxygen supplied to the burner to the amount of oxygen required to convert the octamethylcyclotetrasiloxane and germanium ethoxide through complete combustion to their product oxides of GeO_2 and SiO_2 as demonstrated in the above reaction equations. Without such oxygen delivery, reduced species of germanium and carbon were observed in the soot.

Such delivery rates are preferred in order to provide beneficial attenuation characteristics of the fiber formed by the process. FIG. 2 shows the refractive index profile of the core/clad cane that was made using these preferred delivery rates. FIG. 3 shows the spectral attenuation curve of a 1 kilometer segment of single mode optical fiber of the invention that was made using the preferred delivery rates. It was surprising and unexpected that this method and use of germanium ethoxide and octamethylcyclotetrasiloxane optical waveguide silica feedstocks throughout the soot deposition process would result in an optical fiber with such beneficial characteristics including a loss of only 0.221 dB/km at 1550 nm. This is a particularly good attenuation level for a fiber using new feedstocks. In FIG. 3 the solid curve represents the

spectral attenuation of the inventive optical fiber. For comparison, the dotted curve represents the spectral attenuation of a commercially available Corning SMF-28™ single-mode optical waveguide fiber which was produced using a refined process comprised of the conversion of halide containing feedstocks.

Example 2

An optical waveguide preform was made using a focus burner configuration wherein the octamethylcyclotetrasiloxane and germanium alkoxide fluid feedstock, N_2, and O_2 mixture was delivered through the central fume tube which was surrounded by an N_2 inner shield regulated supply, then a fume shield O_2 regulated supply, then a methane and oxygen premix regulated supply, with N_2 inner shield gas lines and the fume shield O_2 gas lines heated. The GeO_2 doped silica forming liquid feedstock was provided by mixing one part per weight of germanium ethoxide with 3.6 parts per weight of octamethylcyclotetrasiloxane. The optical waveguide preform was made using the following conditions table:

TABLE I

	Core	Clad	Overclad
Mix Ratio $[SiO(CH_3)_2]_4$:$Ge(OC_2H_5)_4$ (by wt.)	3.6:1	1:0	1:0
Delivery Rate of Mixture (g/min)	6	6	7
Carrier N_2 (slpm)	1.25	1.25	1.25
Fume O_2 (slpm)	1.8	1.8	2.4
Inner Shield N_2 (slpm)	3	?	3
Fume Shield O_2 (slpm)	6.8	6.8	5.1
Premix CH_4 (slpm)	1.1	1.1	1.1
Premix O_2 (slpm)	0.9	0.9	1.7
Burner Stoichiometry	0.97		
Deposition Time (min)	240	270	435
Weight of Soot (g)	93	420	1100

The resulting preform was dried and consolidated in a helium and chlorine atmosphere to form a clear glass waveguide preform which was formed into a cane preform. This preform was overcladded using the octamethylcyclotetrasiloxane and burner condition shown in the above table. This overcladded optical waveguide preform was consolidated into an optical fiber preform which was drawn into a fiber. Such a method is most preferred in order to provide beneficial attenuation characteristics. FIG. 4 shows the spectral attenuation curve of this fiber as the solid curve and for comparison the dotted curve represents the spectral attenuation of a Corning SMF-28™ single-mode optical waveguide fiber. As in Example 1, it was surprising and unexpected that such a method of making optical fiber preforms using octamethylcyclotetrasiloxane throughout the soot deposition process along with germanium ethoxide would result in an optical fiber with such beneficial characteristics. This is a particularly good attenuation spectra for a fiber using new feedstocks. This is the most preferred method and feedstock of the invention because of the beneficial attenuation spectra with the fiber being low loss with an attenuation of less than 0.25 db/km at 1550 nm.

Example 3

GeO_2 doped SiO_2 soot was made from a feedstock mixture of germanium methoxide and octamethylcyclotetrasiloxane using the setup shown in FIG. 1. When liquid germanium methoxide and liquid octamethylcyclotetrasiloxane are used they are mixed by weight in a ratio ranging from 1 part germanium methoxide : 3 to 6 parts octamethylcyclotetrasiloxane, preferably 1 part germanium methoxide : 4 to 5 parts octamethylcyclotetrasiloxane. GeO_2 doped SiO_2 soot was made using the following conditions table:

TABLE II

Feedstock Mix Ratio[$SiO(CH_3)_2]_4$:Germanium Methoxide(by wt.)	4.5:1
Delivery Rate of Feedstock Mixture (g/min)	3.6
Carrier N_2 (slpm)	3
Fume O_2 (slpm)	4.5
Inner Shield O_2 (slpm)	2.5
Premix CH_4 (slpm)	2
Premix O_2 (slpm)	1
Outer Shield O_2 (slpm)	2
Burner Stoichiometry	2.4

These conditions resulted in a GeO_2 doped SiO_2 soot which contained 28.7 wt.% GeO_2.

The feedstock compositions of the invention and the method of use in forming optical waveguides are not only beneficial in that chlorine pollutants are not produced during soot deposition, but that chlorine is not incorporated into the soot in that the silicon and germanium components of the feedstocks are free of chlorine to start with. In addition, the absence of chlorine during deposition may improve metal impurity levels in the optical fiber.

It was found that germanium ethoxide when mixed with water is corrosive to metals. It is, therefore, preferred that the germanium ethoxide storage and delivery systems be free of metals, and in particular, it is preferred to use teflon components for parts in contact with the germanium ethoxide particularly when in the liquid state. In doing so, the metal impurities in the consolidated glass are reduced from a few ppm to a few ppb by weight. The germanium ethoxide source liquid used in the invention had metal impurity levels of Fe (<10 ppb), Ni (<10 ppb), Cr (<10 ppb), Cu (<10 ppb), and Al (< 10 ppb). GeO_2 soot

produced from such a liquid pumped through a stainless steel pump had metal impurity levels of Fe (790-2700 ppb), Ni (21-25 ppb), Cr (27-29 ppb), Cu (25-61 ppb), and Al (1300-4500 ppb). GeO_2 soot produced from such a liquid pumped through teflon components had metal impurity levels of Fe (44 ppb), Ni (<10 ppb), Cr (<10 ppb), Cu (<10 ppb), and Al (<10 ppb). Such a non-metallic delivery system resulted in a 10% GeO_2 doped SiO_2 soot of the invention having metal impurities of Fe (14-20 ppb), Ni (<17 ppb), Cr (<10 ppb), Cu (<10 ppb), and Al (<10 ppb). The analysis of a GeO_2 - SiO_2 core of the invention showed metal impurities of Fe (10 ppb), Ni (<5 ppb), Cr (<10 ppb), and V (<10 ppb). The analysis of a SiO_2 clad of the invention showed metal impurities of Fe (10 ppb), Ni (20 ppb), Cr (<10 ppb), and V (<10 ppb). Such low metallic impurity levels are beneficial to the transmission and guiding of light.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents

WE CLAIM:

1. A silica forming feedstock comprised of a siloxane and a germanium alkoxide.

2. A silica forming feedstock as claimed in claim 1 comprised of octamethylcyclotetrasiloxane and a germanium alkoxide.

3. A silica forming feedstock as claimed in claim 1 comprised of octamethylcyclotetrasiloxane and germanium ethoxide.

4. A silica forming feedstock as claimed in claim 1 comprised of octamethylcyclotetrasiloxane and germanium methoxide.

5. A silica forming feedstock consisting essentially of a siloxane and a germanium alkoxide.

6. A silica forming feedstock as claimed in claim 5 consisting essentially of a siloxane and germanium ethoxide.

7. A silica forming feedstock as claimed in claim 6 consisting essentially of octamethylcyclotetrasiloxane and a germanium alkoxide.

8. An optical waveguide silica feedstock consisting of octamethylcyclotetrasiloxane and germanium ethoxide.

9. A germanium doped silica glass formed by the conversion of octamethylcyclotetrasiloxane and germanium ethoxide.

10. A silica forming feedstock comprised of a siloxane and a bimetallic organogermyl.

11. A silica forming feedstock as claimed in claim 10 comprised of a siloxane and digermane.

12. A silica forming feedstock as claimed in claim 10 comprised of a siloxane and di-germoxane.

13. A silica forming feedstock comprised of a siloxane and a germanium alkylalkoxide.

14. A silica forming feedstock comprised of a siloxane and a germanium alkyl.

15. A method of making a low loss optical waveguide preform comprising the steps of:

(a) providing a fluid feedstock comprised of a siloxane and a germanium alkoxide;

(b) delivering said fluid feedstock to a conversion site;

(c) converting said delivered fluid feedstock into GeO_2 doped SiO_2 soot;

(d) depositing said GeO_2 doped SiO_2 soot on a deposition surface; and

(e) forming said deposited GeO_2 doped SiO_2 soot into an optical waveguide preform.

16. A method as claimed in claim 15, wherein the step of providing a fluid feedstock comprised of a siloxane and a germanium alkoxide further comprises the step of providing a fluid feedstock comprised of octamethylcyclotetra-siloxane and germanium alkoxide.

17. A method as claimed in claim 16, wherein the step of providing a fluid feedstock comprised of octamethylcyclotetrasiloxane and germanium alkoxide further comprises the step of providing a fluid feedstock comprised of octamethylcyclotetrasiloxane and germanium ethoxide.

18. A method as claimed in claim 17, wherein the step of providing a fluid feedstock comprised of octamethyl-cyclotetrasiloxane and germanium ethoxide further comprises the step of mixing liquid octamethylcyclo-tetrasiloxane with liquid germanium ethoxide.

19. A method as claimed in claim 18, wherein the step of delivering said fluid feedstock further comprises the step of vaporizing said fluid feedstock.

20. A method as claimed in claim 15, wherein the step of forming said deposited GeO_2 doped SiO_2 soot into an optical waveguide preform further comprises the step of cladding said GeO_2 doped SiO_2 soot with SiO_2.

21. A method as claimed in claim 20, wherein the step of cladding said GeO_2 doped SiO_2 soot with SiO_2 further comprises the steps of providing a fluid feedstock comprised of a siloxane, delivering said fluid siloxane feedstock to a conversion site, and converting said delivered fluid siloxane feedstock into SiO_2 soot.

22. A method of making a low loss optical waveguide fiber comprising the steps of:

(a) providing a fluid feedstock comprised of a siloxane and a germanium alkoxide;

(b) delivering said fluid feedstock to a conversion site;

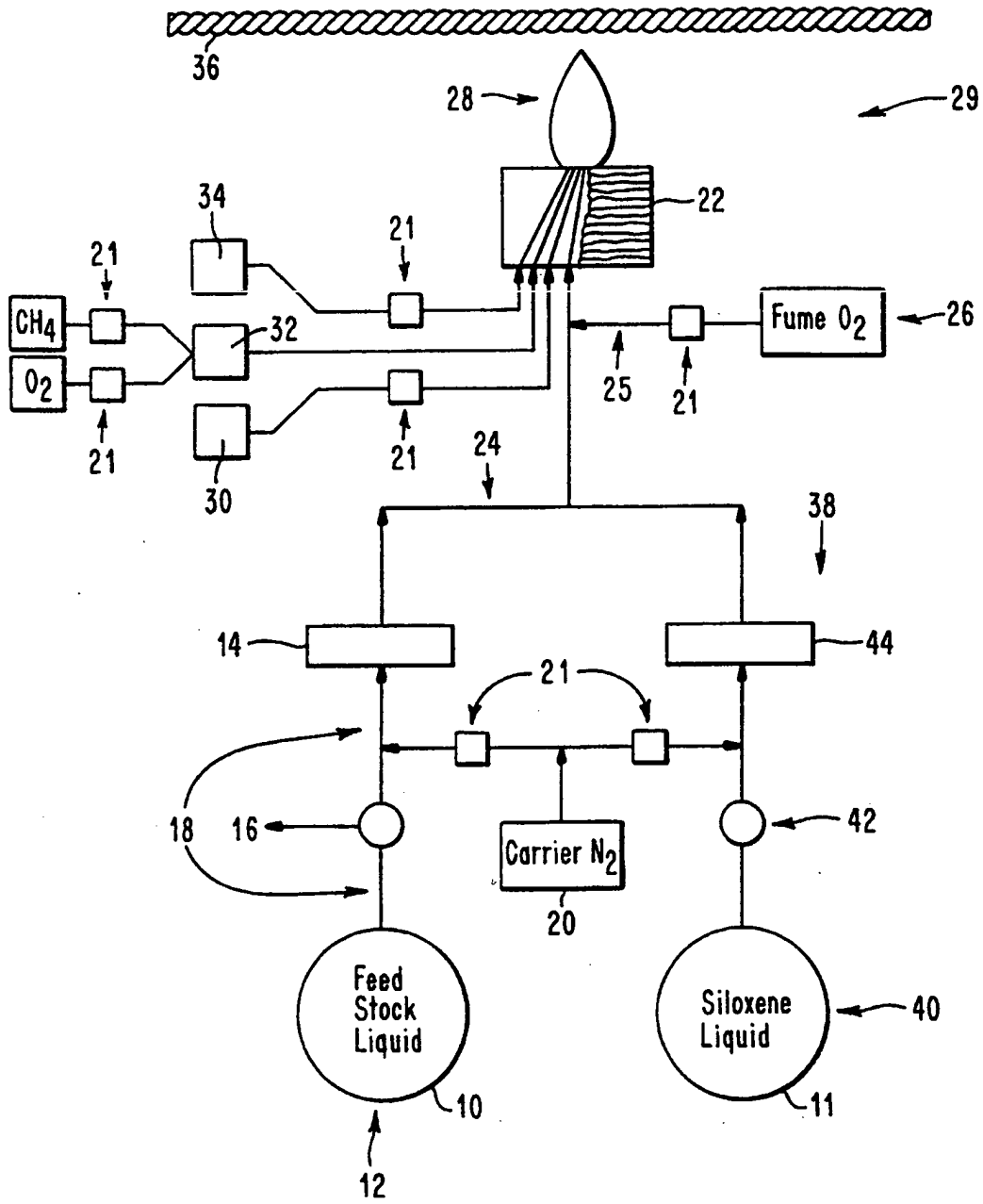
(c) converting said delivered fluid feedstock into GeO_2 doped SiO_2 soot;

(d) depositing said GeO_2 doped SiO_2 soot on a deposition surface;

(e) forming said deposited GeO_2 doped SiO_2 soot into an optical waveguide preform; and

(f) drawing said optical waveguide preform into a fiber.

FIG. 1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28
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CH_4
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Fume O_2
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O_2
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21
30
24
38
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21
18
16
Carrier N_2
42
20
Feed Stock Liquid
Siloxene Liquid
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10
11
12

FIG. 2

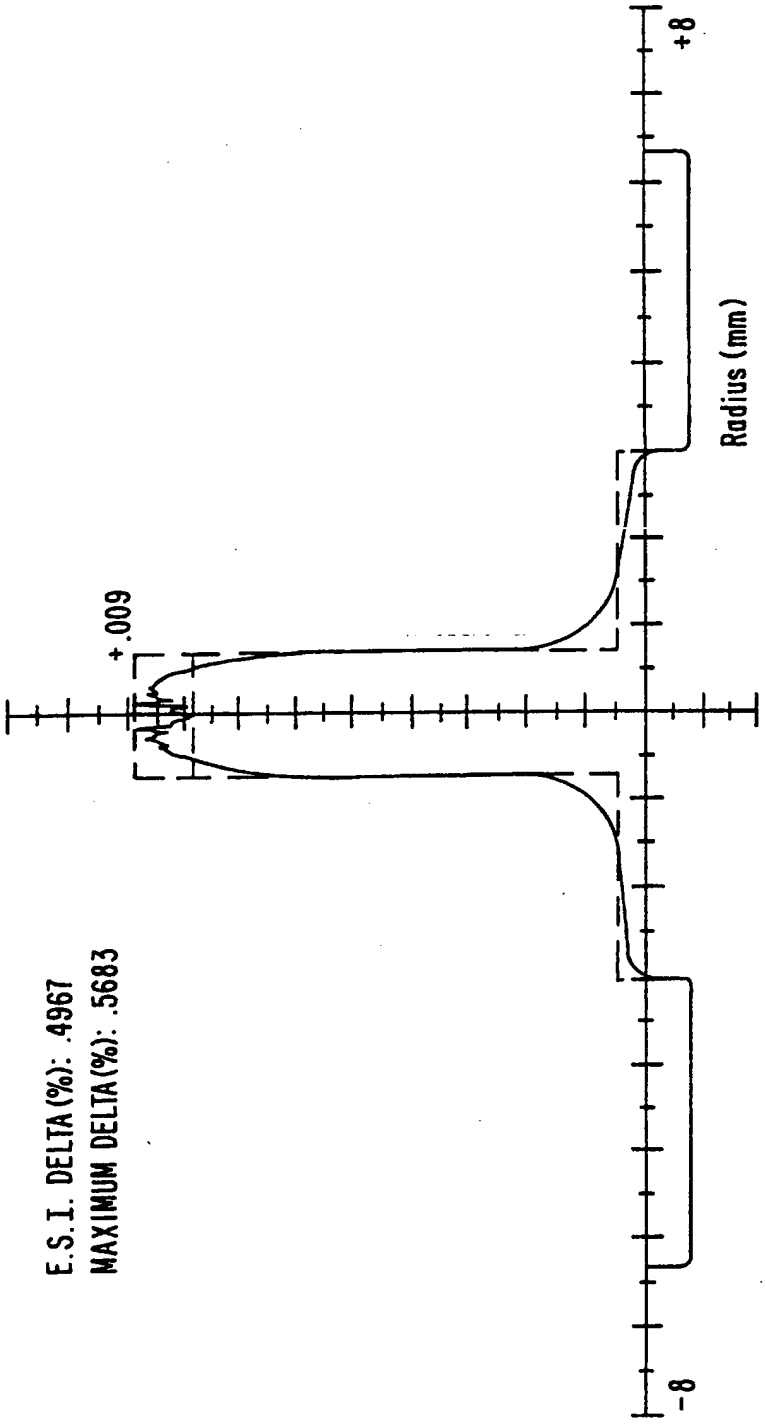
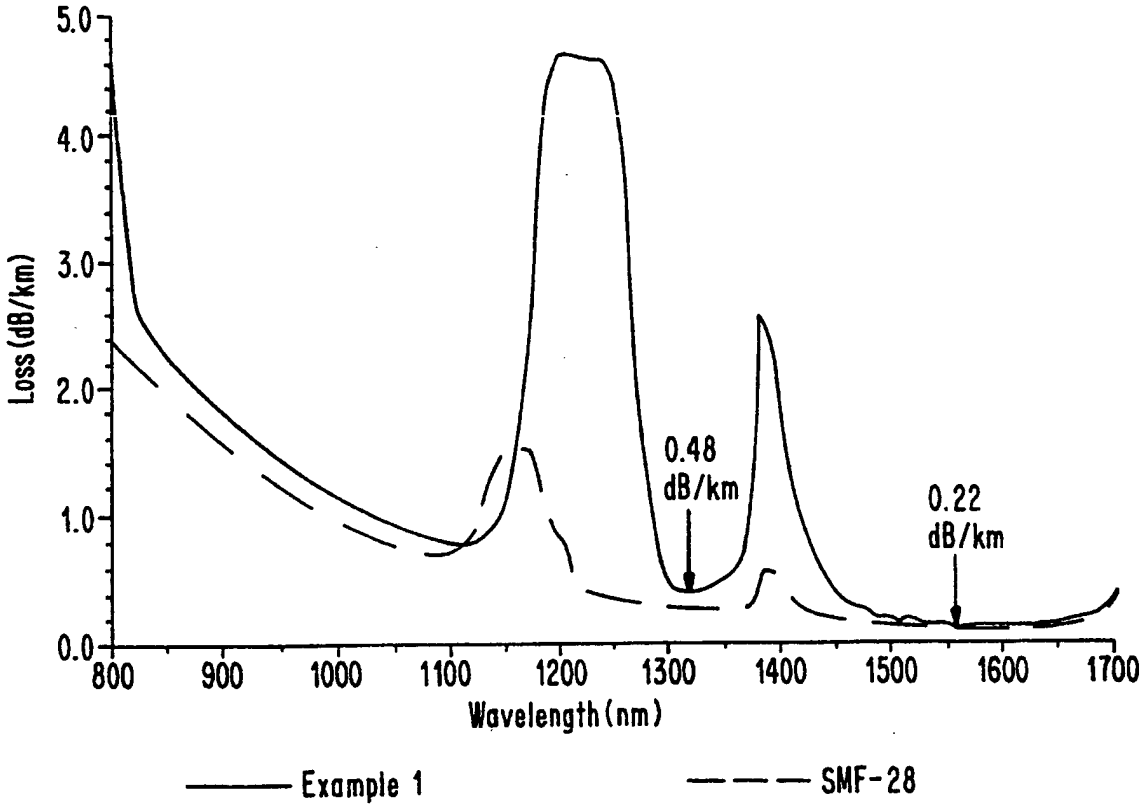


FIG. 3


5.0
4.0
3.0
2.0
1.0
0.0
Loss (dB/km)
800
900
1000
1100
1200
1300
1400
1500
1600
1700
Wavelength (nm)
0.48
dB/km
0.22
dB/km
Example 1
SMF-28

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/23123

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08G 77/398; B29D 11/00; G02B 6/00
US CL :528/33; 264/1.29; 385/141

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/33; 264/1.29; 385/141

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS
search terms: germanium and cyclic siloxane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 5,324,539 A (MAEDA et al.) 28 June 1994, see entire reference.	1-14 — 15-22
A	US 5,548,051 A (MICHALCZYK et al.) 20 August 1996, see entire reference.	1-22
A	US 5,527,871 A (TANI et al.) 18 June 1996, see entire reference.	1-22

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 13 MARCH 1998	Date of mailing of the international search report 10 APR 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer MARGARET GLASS Telephone No. (703) 308-2351

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